Homogenizing fibre optic for plasma emission in multichannel LIBS spectrometry

J. F. Algorri[a,b,c], M. G. Fernández-Manteca[c], L. Rodriguez-Cobo[a,b,c], J.M López-Higuera[a,b,c], and A. Cobo[a,b,c]

[a]Photonics Engineering Group, Universidad de Cantabria, 39005, Santander, Spain
[b]CIBER-bbn, Instituto de Salud Carlos III, 28029, Madrid, Spain
[c]Instituto de Investigación Sanitaria Valdecilla (IDIVAL), 39011, Santander, Spain

ABSTRACT

In this work, we propose a novel approach for plasma collection in Laser-Induced Breakdown Spectroscopy (LIBS). Our method aims to achieve better homogenization than traditional methods, especially in the context of a heterogeneous plume.

Keywords: Spectrocsopy, LIBS, optical fiber

1. INTRODUCTION

Laser-Induced Breakdown Spectroscopy (LIBS) is a method that analyzes the composition of a sample at the atomic level using spectral analysis of the plasma induced by a pulsed laser.[1] However, shot-to-shot variations in the plasma plume's position, morphology, and electronic temperature and density make it challenging to capture the optical emission for spectral analysis. This can cause a loss in sensitivity and inaccuracies in chemical imaging. Different optical solutions have been proposed to overcome these challenges, including the use of a single or multiple-lens arrangement, a pierced parabolic mirror, or an optical fibre. Multichannel CCD spectrometers require a bundle of optical fibres to split the captured plasma emission, which can cause "spectral artifacts" due to changes in light-splitting efficiency. The term spectral artifacts refers to undesired variations in amplitude between different spectral ranges of a captured spectrum, which cannot be attributed to naturally occurring changes in plasma emission.[2] Rather, these variations result from changes in the light splitting performed by the collection optics, which affect the capturing efficiencies of each channel. Proposed solutions include the use of a fibre homogenizer (a short silica rod placed in front of the fibre bundle, typically about 5 cm in length) or a Köhler configuration. In the latter case, the Köhler configuration, also known as Köhler illumination, is a technique used in microscopy to achieve a uniform and optimal illumination of the specimen being observed. It was developed by August Köhler in the late 19th century and is widely used in modern microscopy. The main goal of Köhler illumination is to provide even illumination across the specimen while minimizing artifacts and maximizing image quality. It involves careful adjustment of the light source, condenser, and aperture diaphragm to achieve this desired illumination. Also, it has been proposed recently as a homogenizer in LIBS.[3] In previous work,[2] we presented a complete assessment of the performance of various collection optics in terms of capturing efficiency and channel-to-channel variations involving a multichannel spectrometer. According to this work, even the most effective method for minimizing shot-to-shot inter-channel differences (using a long single-core optical fibre without extra lenses) still results in some minor yet noticeable spectral artifacts.

This work presents a complete study of one of the most effective approaches to homogenising plasma emission (a silica rod placed in front of the fibre bundle). The study's main limitations reside in the number of steps and rays per emitter. Different lengths, wavelengths and plume shifts are studied, showing that there is still a considerable coefficient of variation in the amplitude responses. In addition, an approach to achieve better homogenization for a plasma collection with a heterogeneous plume is also proposed and analysed. The results show that a square section is preferred to reduce the effect of a heterogeneous emission. However, there is still a certain amount of inevitable variation from fibre to fibre.

Further author information: (Send correspondence to J.F.A.)
J.F.A.: E-mail: algorrijf@unican.es

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2. EFFECTS OF HOMOGENIZER LENGTH AND PLUME WAVELENGTH AND DRIFT

The model considers a silica fibre optic with a 1 mm core. The parameters for silica from 0.21 to 6.7 μm are extracted from.[4] The plasma plume is modelled as a group of discrete emitters with a conical emission angle of $\pi/30$ separated 250 μm. The total size of the plasma plume is 1 mm in width and 2 mm in height, and it is positioned 2 mm away from the fibre homogenizer. The structure is analyzed using ray tracing, with a total of 45 emitters with 1000 rays each and a total power of 1W. The fibre bundle is designed for an 8-channel spectrometer and is connected in direct contact with the fibre homogenizer end. A schematic depiction of the resulting structure is shown in Figure 1(a).

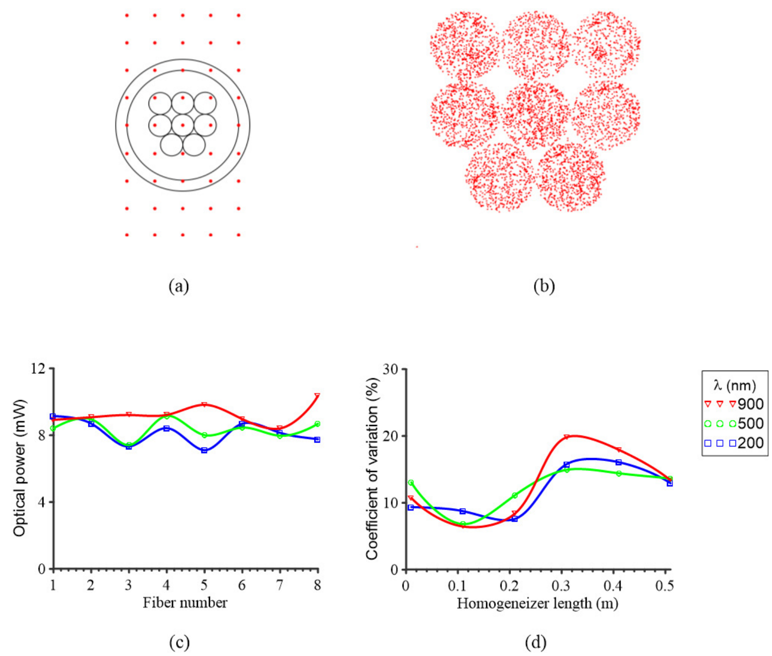

Figure 1. (a) Model of the proposed structure. (b) Spot diagram (length 1cm, wavelength 200 nm). (c) The optical power at different fibres for 11 cm length. (d) Coefficient of variation between fibres as a function of homogenizer length.

As shown in the spot diagram of Figure 1(b), the rays have been effectively distributed among each bundle even with a 1 cm homogenizer (200 nm of wavelength). Figure 1(c) shows the optical power in each bundle fibre for 11 cm length and several wavelengths. To analyze this variation, the coefficient of variation (standard deviation/mean) between 1 cm to 51 cm is displayed in Figure 1(d). The results for a homogeneous plasma plume centred at the input of the fibre homogenizer reveal that for a wavelength of 200 nm, the variation has a minimum of around 20 cm and it saturates around 15% for lengths higher than 30 cm. For the other wavelengths, the minimum is at 10 cm and tends to reach a saturation point of 15% for longer lengths. The mean value of the 3 wavelengths, Figure 2(c) blue line, indicates that a fibre length of around 10 cm is the optimum for this application (7% of variation), and the region between 10 cm to 30 cm is the most variant with respect to different wavelengths.

One problem with measuring the plasma plume in LIBS is that it can shift during the measurement process. This phenomenon is known as "plasma plume drift," and it can occur due to a variety of factors, including air currents, temperature gradients, and other physical and chemical effects in the sample. Plasma plume drift can have a significant impact on the accuracy and precision of LIBS measurements, especially when analyzing complex samples or performing depth profiling. To minimize the effects of plasma plume drift, researchers often use specialized techniques, such as time-resolved spectroscopy or double-pulse LIBS, that can account for changes in the plasma plume over time. In this case, in order to evaluate the effect of the plume drift, the emitters are displaced 0.25 mm and 0.5 mm from the centre on the x-axis. In Figure 2(a) it can be seen the model with a shift of 0.5 mm. As shown in Figure 2(b) the number of rays that reach the fibre bundle is less but still shows a good homogenization (a 1 cm length homogenizer and 200 nm of wavelength is considered). Figure 2(c) includes the mean coefficient of variation for the three analysed wavelengths (200 nm, 500 nm and 900nm) at three different positions. The results indicate a minimum of around 10 cm for small shifts (7% of variation). For a shift of 0.5 cm, the coefficient of variation is generally high (around 15%). In conclusion, for a homogeneous plume centred in the fibre optic homogenizer and small drifts, the optimum length is around 10 cm.

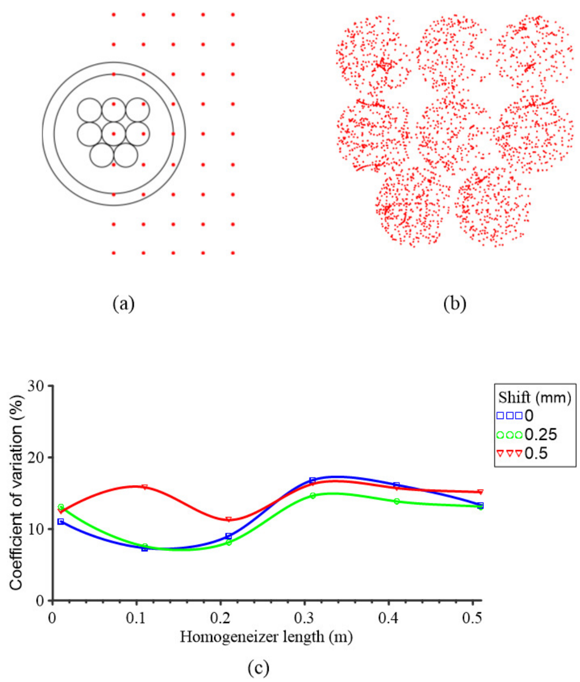

Figure 2. (a) Model of the proposed structure. (b) Spot diagram (length 1cm, wavelength 200 nm). (c) Mean for 3 wavelengths of the coefficient of variation between fibres as a function of length.

3. A SQUARE SECTION HOMOGENEIZER

A square silica homogenizer (1 mm width) is proposed to improve the homogenization. For a homogeneous plume centred in the homogenizer input, the coefficient of variation study for several lengths and wavelengths reveal a slightly better behaviour to a circular section, particularly for longer lengths. The mean of the coefficient of variation has a minimum of 7% around 10 cm and tends to converge for lengths longer than 30 cm at 8%.

Despite this, it has to be considered that the plume in LIBS is typically heterogeneous. When a laser is used to ablate a sample, the plasma plume that is generated is composed of particles that come from different regions of the sample. These particles have different temperatures, ionization states, and densities, which can cause the plasma plume to be spatially and temporally heterogeneous. This can lead to shot-to-shot variations in the LIBS signal, which can be problematic for quantitative analysis. To model this effect, only one emitter with 1000 rays and a total power of 1W is placed at three different positions on the y-axis, see the red point in the fibre bundle of Figure 3 (a). As can be observed in Figure 3 (c), the circular section homogenizer has a considerable variation in the optical power between fibres. In contrast, the square section homogenizer distributes the power more homogeneously. Specifically, the circular area has a 42%, 47 % and 69 % of coefficient of variation for the emitter placed at position -0.25 mm, 0, and 0.25 mm (y-axis), respectively. On the other hand, the square section has a 22%, 10 % and 28 % of coefficient of variation for the emitter placed at position -0.25 mm, 0, and 0.25 mm (y-axis), respectively. In conclusion, the square section responds better to both homogeneous and heterogeneous plume emissions. In the latter case, the coefficient of variation is less than half but still has non-negligible values.

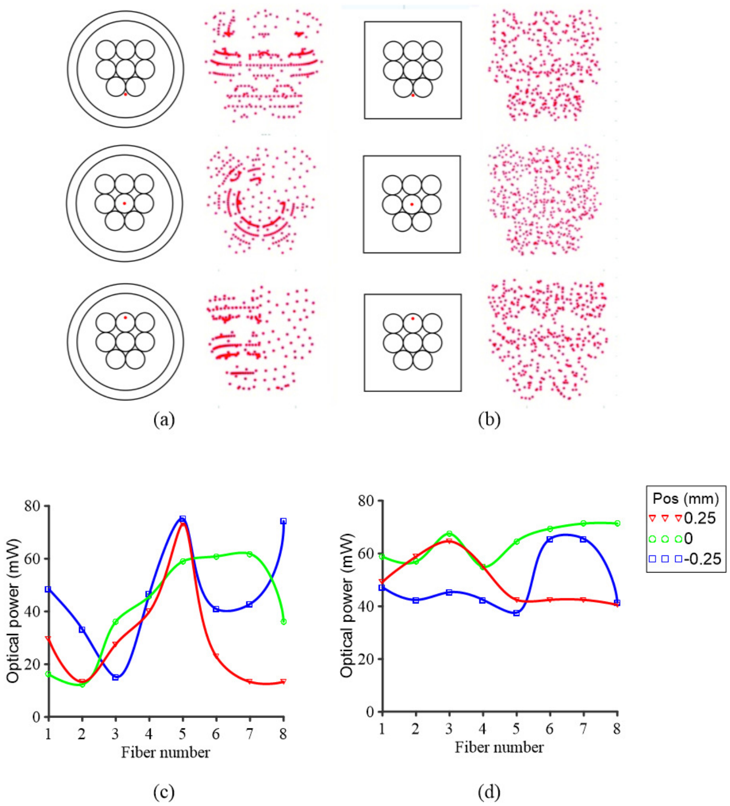

Figure 3. Model of the proposed structure and spot diagram (length 1cm, wavelength 200 nm) for (a) circular (b) square. The optical power at different fibres for 11 cm length, (c) circular (d) square.

4. CONCLUSIONS

This work presents a comprehensive study on optical fiber homogenizers for plasma plumes in LIBS. Various lengths, wavelengths, and plume drifts have been considered, demonstrating that a considerable coefficient of variation remains in the amplitude responses. For heterogeneous plume emissions, the responses are even worse. To address this, a square-section approach has been proposed and analyzed to improve homogenization in plasma collection with a heterogeneous plume. The results indicate that a square section is preferable for reducing the effects of heterogeneous emission. However, some inevitable variation between fibers still persists.

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